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PATENT ABSTRACTS OF JAPAN

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(54) SILICONE FOAM AND METHOD FOR PRODUCING THE SAME

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a silicone foam having a small pore size, excellent rigidity and excellent heat insulation, and to provide a method for producing the silicone foam by which the silicone foam can be produced in a state that the change of the volume is small before and after the foamed is formed.
SOLUTION: This method for producing the silicone foam is characterized by comprising the first process for obtaining a water-in-oil type emulsion curing raw material comprising 100 pts. wt. of an alkenyl group-containing organopolysiloxane, 1 to 300 pts. wt. of a surfactant, 0.1 to 50 pts. wt. of a hydrogen organopolysiloxane, 20 to 1,500 pts. wt. of water, and a platinum group element catalyst, the second process for heating the water-in-oil type emulsion curing raw material to subject the water-in-oil type emulsion curing raw material and the hydrogen organopolysiloxane in the oil layer to an addition reaction to obtain the wet silicone foam, and the third process for removing the water from the wet silicone foam to obtain the silicone foam.

CLAIMS

[Claim(s)]
[Claim 1]
Alkenyl-group content organopolysiloxane 100 weight section, one to surface-active agent 300 weight section, The 1st process of obtaining a W / O type emulsion hardening raw material including 0.1 to hydrogen organopolysiloxane 50 weight section, 20 to water 1500 weight section, and a platinum group system catalyst, Heat this W / O type emulsion hardening raw material, and the addition reaction of said alkenyl-group content organopolysiloxane and said hydrogen organopolysiloxane in an oil reservoir is carried out, A manufacturing method of silicone foam including the 3rd process of removing moisture in silicone foam of the 2nd process of obtaining silicone foam of a damp or wet condition, and this damp or wet condition, and obtaining silicone foam.
[Claim 2]
Said 1st process Alkenyl-group content organopolysiloxane 100 weight section, One to surface-active agent 300 weight section, Hydrogen organopolysiloxane 0.1 - 50 weight sections are added in the 1st (a) process and this W / O type emulsion reserve raw material which obtain a W / O type emulsion reserve raw material including 20 to water 1500 weight section, and a platinum group system catalyst. A manufacturing method of the silicone foam according to claim 1 consisting of the 1st (b) process of obtaining a W / O type emulsion hardening raw material.
[Claim 3]
A manufacturing method of the silicone foam according to claim 1 or 2, wherein said surface-active agent is hydrophilic radical denaturation organopolysiloxane.
[Claim 4]
Said hydrophilic radical denaturation organopolysiloxane Carbinol modified silicone oil, A manufacturing method of the silicone foam according to claim 3 being at least one sort of silicone oil chosen from a group which consists of polyether modified silicone oil, epoxy modified silicone oil, and carboxyl modified silicone oil.
[Claim 5]
Silicone foam, wherein density is 0.10-0.80g[/cm] ^{3} and an average pore diameter is 5-100 micrometers.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]
This invention relates to silicone foam suitably used as shock absorbing material or thermal insulation, and a manufacturing method for the same.
[0002]
[Description of the Prior Art]
Conventionally, various methods are known as a manufacturing method of silicone foam. For example, the method of obtaining silicone foam by making it harden using silicone rubber of the kind in which it foams at the time of hardening, The method (JP,H7-122000,B) of making it foam by generating of the steam at the time of heating is known by using the aquosity emulsion containing the water and the viscous agent as alkenyl-group content organopolysiloxane, an emulsifier, and a foaming agent as a base.
[0003]
[Problem to be solved by the invention]
However, in the method to which the above gases are made to foam, since the path of the stoma in silicone foam was as large as about hundreds-1000 micrometers, rigidity and adiathermancy became insufficient easily. In order to make it foam with a gas, the problem that it was large and shaping with a mold was difficult also had a volume change before and behind foam curing. In order to make it foam with a gas, there was a problem that dispersion in the size of a stoma was large and it was difficult to control in a uniform size.
[0004]
Therefore, the purpose of this invention is to provide the manufacturing method of the silicone foam which can be manufactured in the state where the size of a stoma is small, and a volume change is small before and after form forming the silicone foam which is excellent in rigidity and adiathermancy, and this silicone foam.
[0005]
[Means for solving problem]
As a result of inquiring wholeheartedly, this invention persons in this actual condition Alkenyl-group content organopolysiloxane, The size of a stoma is small, when a W / O type emulsion hardening raw material including a surface-active agent, hydrogen organopolysiloxane, water, and a platinum group system catalyst is heated and the addition reaction of alkenyl-group content organopolysiloxane and hydrogen organopolysiloxane in an oil reservoir is carried out, Before and after form forming the silicone foam which is excellent in rigidity and adiathermancy, a volume change finds out that it can manufacture in the small state, and came to complete this invention.
[0006]
This invention Namely, alkenyl-group content organopolysiloxane 100 weight section, One to

surface-active agent 300 weight section, 0.1 to hydrogen organopolysiloxane 50 weight section, The 1st process of obtaining a W / O type emulsion hardening raw material including 20 to water 1500 weight section, and a platinum group system catalyst, Heat this W / O type emulsion hardening raw material, and the addition reaction of said alkenyl-group content organopolysiloxane and said hydrogen organopolysiloxane in an oil reservoir is carried out, The manufacturing method of silicone foam including the 3rd process of removing the moisture in the silicone foam of the 2nd process of obtaining the silicone foam of a damp or wet condition, and this damp or wet condition, and obtaining silicone foam is provided.

[0007]

As for this invention, density provides silicone foam, wherein 0.10 - 0.80 g/cm^3 and an average pore diameter are 5-100 micrometers.

[0008]

[Mode for carrying out the invention]

The 1st process is a process of obtaining a W / O type emulsion hardening raw material including alkenyl-group content organopolysiloxane, a surface-active agent, hydrogen organopolysiloxane, water, and a platinum group system catalyst.

[0009]

The alkenyl-group content organopolysiloxane used by this invention is the following average composition formula (1).

$R^1{}_nSiO_{(4-n)/2}$ (1)

(-- substitution that the inside of a formula and R^1 are the same, or of a different kind or an unsubstituted monovalent hydrocarbon group, and n -- 1.95-2.08 -- it is a positive number of 1.98-2.02 preferably.) -- it is organopolysiloxane shown and has the alkenyl group combined with an average of two or more silicon atoms in the molecule.

[0010]

R^1 is the carbon numbers 1-12 combined with the silicon atom especially the substitution of 1-8, or an unsubstituted monovalent hydrocarbon group here, For example, a methyl group, an ethyl group, a propyl group, an isopropyl group, a butyl group, An isobutyl group, a tert-butyl group, a pentyl group, a neopentyl group, Alkyl groups, such as a hexyl group, a heptyl group, an octyl group, a nonyl group, a decyl group, and dodecyl, Cycloalkyl groups, such as a cyclopentylic group, a cyclohexyl group, and a cycloheptyl group, A vinyl group, an allyl group, a propenyl group, an isopropenyl group, a butenyl group, Alkenyl groups, such as an isobutenyl group, a hexenyl group, and a cyclohexenyl group, Aryl groups, such as a phenyl group, a tolyl group, a xylyl group, a naphthyl group, and a biphenyl group, The chloromethyl group by which some or all of the hydrogen atom in aralkyl groups, such as benzyl, a phenylethyl group, a phenylpropyl group, and a methylbenzyl group, or these hydrocarbon groups was replaced by halogen atoms, cyano groups, etc., such as F, Cl, and Br, 2-bromoethyl group, a 3,3,3-trifluoropropyl group, 3-chloropropyl group, a cyanoethyl group, etc. are mentioned.

[0011]

In this case, at least an average of two in the substitution shown by the above-mentioned R^1 or an unsubstituted monovalent hydrocarbon group are an alkenyl group, and, as for especially the quantity of an alkenyl group, 0.001-0.1 mol is preferred 0.0001-1 mol in the alkenyl-group content organopolysiloxane 100g. It may combine with the silicon atom of molecular chain terminals, or may combine with the silicon atom in the middle of a chain, and an alkenyl group may exist in both.

[0012]

As for n, it is preferred among the above-mentioned formula (1) 1.95-2.08, and that it is a positive number of 1.98-2.02 preferably, and the molecular structure of this alkenyl-group content organopolysiloxane is straight chain shape which consists of a repetition of JIORUGANO siloxane units. Although it is preferred that it is what has an alkenyl group in chain both ends at least, it may

have the branched state structure which includes $R^1SiO_{3/2}$ unit, and $SiO_{4/2}$ unit in a part. As for this alkenyl-group content organopolysiloxane, it is preferred that those molecular chain terminals are blocked by bird organosilyl groups, such as trivinylsilyl, methyldi vinylsilyl, dimethylvinylsilyl, or a trimethylsilyl group.

[0013]

It is usually 25 or more cSt at 25 **, and since emulsion-izing according that it is 250 - 10,000cSt still more preferably to churning is preferably easy for the viscosity of this alkenyl-group content organopolysiloxane 25 to 500,000 cSt, it is preferred.

[0014]

As a surface-active agent used by this invention, hydrophilic radical denaturation organopolysiloxane is mentioned, for example. Here, hydrophilic radical denaturation organopolysiloxane means the organopolysiloxane which has hydrophilic radicals, such as a hydroxyl group and an organic group which has an ether bond. Since alkenyl-group content organopolysiloxane and hydrogen organopolysiloxane which are contained in an oil reservoir in this invention as the hydrophobic part of a surface-active agent is organopolysiloxane, and compatibility are good, it is desirable. At least one sort chosen from the group which consists of carbinol modified silicone oil, polyether modified silicone oil, epoxy modified silicone oil, and carboxyl modified silicone oil as such hydrophilic radical denaturation organopolysiloxane, for example is mentioned.

[0015]

As for hydrophilic radical denaturation organopolysiloxane, if only the both ends or one end of a molecule denaturalizes by a hydrophilic group, in order that hydrophilic radical denaturation organopolysiloxane may show the dispersion effect of the waterdrop by steric exclusion, the form of independent stoma structure will become is easy to be obtained. On the other hand, if the side chain of a molecule denaturalizes by a hydrophilic group, hydrophilic radical denaturation organopolysiloxane has the weak electrostatic repulsion between waterdrop, and since waterdrop adjoins and exists in an emulsion, the form of continuation stoma structure will become is easy to be obtained. Therefore, what is necessary is just to choose the kind of hydrophilic radical denaturation organopolysiloxane suitably according to the stoma structure expected to the silicone foam to manufacture.

[0016]

although HLB of a surface-active agent is not what is limited especially since a W / O type emulsion hardening raw material should just be obtained as a result in this invention -- usually -- 0-6 -- it is 0-4 preferably.

[0017]

The viscosity at 25 ** of a surface-active agent is usually 10 - 1000cSt preferably ten to 30000 cSt. When viscosity is in this within the limits, since emulsion-izing by churning is easy, it is desirable.

[0018]

The hydrogen organopolysiloxane used by this invention, It is organopolysiloxane which has at least two SiH groups (namely, hydrogen atom combined with the silicon atom) in one molecule, Although it may be any of straight chain shape, annular, branched state, and three-dimensional network structure and the publicly known ORGANO hydrogen polysiloxane can be used as a hardening agent (cross linking agent) of an addition reaction hardening type silicone rubber composition, it is usually the following average composition formula (2).

$R^2{}_aH_bSiO_{(4-a-b)/2}$ (2)

the inside of a formula and R^2 are the same as that of the above-mentioned R^1 -- desirable -- the carbon numbers 1-12 -- especially -- the alkyl group of 1-8. It is an alkenyl group, an aryl group, an aralkyl group, and unsubstituted or the substitution monovalent hydrocarbon group of these halogenation objects, and what does not contain aliphatic unsaturated bonds is preferred, and a

methyl group, a phenyl group, and a 3,3,3-trifluoropropyl group are preferred especially. a and b are 0.802<=a+b<=3 and a positive number which fills 1.01 <=a+b<=2.5 with 1<=a<=2 and 0.01<=b<=1 preferably in 0.8<=a<=2.2 and 0.002<=b<=1. What is shown can be used.

[0019]

Although it has preferably the three or more above-mentioned SiH groups in [at least two] one molecule, this may be in molecular chain terminals, or there may be in the middle of a chain. Since emulsion-izing according that the viscosity at 25 ** is especially 1 - 1,000cSt one to 10,000 cSt to churning is easy for the ORGANO hydrogen polysiloxane, it is preferred. As for especially the ORGANO hydrogen polysiloxane, it is preferred that the 2-500 number of degrees of polymerization, i.e., the silicon atom in one molecule, is 4-200.

[0020]

The platinum group system catalyst used by this invention is a catalyst for carrying out the addition reaction of the silicon atom absorbed water matter atom in hydrogen organopolysiloxane to the alkenyl group of alkenyl-group content organopolysiloxane. As a platinum group system catalyst, there are the metal simple substance and compound of a platinum group, and a publicly known thing can be conventionally used for this. For example, the particle-like platinum metal made to adsorb on platinum black, silica, alumina, or a carrier like silica gel, A complex with platinic chloride, chloroplatinic acid, and chloroplatinic acid 6 monohydrate, an olefin, or divinyl dimethylpolysiloxane, the alcohol solution of chloroplatinic acid 6 monohydrate, a palladium catalyst, a rhodium catalyst, etc. are mentioned.

[0021]

In the 1st process, the above-mentioned alkenyl-group content organopolysiloxane, a surface-active agent, hydrogen organopolysiloxane, water, and a platinum group system catalyst are mixed, and the W / O type emulsion hardening raw material containing these is obtained. In this invention, say a W / O type emulsion hardening raw material, and the raw material of the heat cure of the 2nd process specifically, It is a mixture including alkenyl-group content organopolysiloxane, a surface-active agent, hydrogen organopolysiloxane, water, and a platinum group system catalyst, and what presents a W / O type emulsion is said.

[0022]

It is not limited, and may dissolve, for example in a suitable order for water, and especially mixed sequence forewords, such as alkenyl-group content organopolysiloxane in the case of preparation of a W / O type emulsion hardening raw material, may mix these simultaneously. However, as for hydrogen organopolysiloxane, since it is easy to hydrolyze if water is contacted, it is preferred to contact hydrogen organopolysiloxane and water just before the 2nd process.

[0023]

Thus, as a method of making it contacting just before the 2nd process, hydrogen organopolysiloxane and water, In the 1st process, first specifically Alkenyl-group content organopolysiloxane, The 1st (a) process of mixing a surface-active agent, water, and a platinum group system catalyst, and obtaining a W / O type emulsion reserve raw material is performed, Next, the method of performing the 1st (b) process of adding hydrogen organopolysiloxane in this W / O type emulsion reserve raw material, and obtaining a W / O type emulsion hardening raw material is mentioned. In this invention, a W / O type emulsion reserve raw material is a mixture including alkenyl-group content organopolysiloxane, a surface-active agent, water, and a platinum group system catalyst, and what presents a W / O type emulsion is said.

[0024]

As a mixing method in the case of preparation of a W / O type emulsion hardening raw material or a W / O type emulsion reserve raw material, Although it may carry out using a common agitator, since generation of a W / O type emulsion hardening raw material or a W / O type emulsion reserve raw material will be promptly performed if emulsion machines, such as a homogenizer, are used, it is desirable.

[0025]
The loadings of the surface-active agent in a W / O type emulsion hardening raw material are usually five to 100 weight section preferably one to 300 weight section to alkenyl-group content organopolysiloxane 100 weight section. When the loadings of a surface-active agent are in this within the limits, since it is easy to obtain a W / O type emulsion, it is desirable.
[0026]
The loadings of hydrogen organopolysiloxane in a W / O type emulsion hardening raw material are usually 0.1 to 50 weight section to alkenyl-group content organopolysiloxane 100 weight section. When the loadings of hydrogen organopolysiloxane are in this within the limits, since the mechanical strength of silicone foam and heat resistance which are obtained become high enough, it is desirable.
[0027]
In a W / O type emulsion hardening raw material, the rate of a compounding ratio of alkenyl-group content organopolysiloxane and hydrogen organopolysiloxane, The rate of the hydrogen atom combined with the silicon atom in hydrogen organopolysiloxane to one alkenyl group combined with the silicon atom in alkenyl-group content organopolysiloxane is usually 0.5-10 pieces, and is 1-4 pieces preferably. When the rate of a compounding ratio is in this within the limits, since the mechanical strength of silicone foam and heat resistance which are obtained become high enough, it is desirable.
[0028]
The loadings of the water in a W / O type emulsion hardening raw material are usually 100 to 300 weight section preferably 20 to 1500 weight section to alkenyl-group content organopolysiloxane 100 weight section. When the loadings of water are in this within the limits, since it is easy to obtain a W / O type emulsion and the voidage of the silicone foam obtained becomes large easily, it is desirable. Although it is it easy to obtain a W / O type emulsion that the loadings of water are less than 100 weight sections, since form becomes hard easily when voidage becomes small, it is not desirable. If the loadings of water exceed 300 weight sections, although voidage becomes large and can produce soft form, since it is difficult to get, it is not desirable in a W / O type emulsion.
[0029]
Although a publicly known quantity of the grade which can promote an addition reaction may be sufficient as the loadings of the platinum group system catalyst over a W / O type emulsion hardening raw material, the concentration after adding in a W / O type emulsion hardening raw material is the quantity converted into the amount of platinum metals, and it is made to usually be set to 0.5-1000 ppm, for example. When the loadings of a platinum group system catalyst are in this within the limits, an addition reaction is usually fully promoted, and since it is economical, it is desirable.
[0030]
If the 1st process is performed, the liquefied or creamy W / O type emulsion hardening raw material which has alkenyl-group content organopolysiloxane, hydrogen organopolysiloxane, and a platinum group system catalyst in an oil reservoir will generate. Water is contained in the water layer distributed in an oil reservoir, and the above-mentioned surface-active agent exists in an interface. the -- the liquefied or creamy W / O type emulsion hardening raw material which has alkenyl-group content organopolysiloxane and a platinum group system catalyst in an oil reservoir generates the W / O type emulsion reserve raw material obtained after 1(a) process.
[0031]
The 2nd process is a process of heating the above-mentioned W / O type emulsion hardening raw material, stiffening said alkenyl-group content organopolysiloxane and said hydrogen organopolysiloxane in an oil reservoir, and obtaining the silicone foam of a damp or wet condition.
[0032]
50-100 ** of cooking temperature is usually 60-80 ** preferably. When cooking temperature is in

this within the limits, since volatilization of water before an oil reservoir hardens can be controlled, it is desirable. Since the stoma generated in form when water boils will become big and rough if 100 ** is exceeded, cooking temperature is not preferred. It is not desirable in order to take a long time for an oil reservoir to harden that cooking temperature is less than 50 **. Cooking time is usually 0.5 to 3 hours preferably for 0.5 to 10 hours.

[0033]

If the 2nd process is performed, the silicone foam of a damp or wet condition will be obtained. In order that alkenyl-group content organopolysiloxane and hydrogen organopolysiloxane in the oil reservoir of a W / O type emulsion hardening raw material may carry out the addition reaction of the silicone foam of this damp or wet condition as it is and may harden it, it originates in a water layer -- abbreviated -- the silicone foam which has a stoma of a uniform size is obtained. If the hydrophilic radical denaturation organopolysiloxane in which only the both ends or one end of the molecule denaturalized by the hydrophilic group is used for silicone foam as a surface-active agent as mentioned above, the stoma structure of silicone foam will turn into independent stoma structure easily. If the side chain of a molecule uses the hydrophilic radical denaturation organopolysiloxane which denaturalized by the hydrophilic group, the stoma structure of silicone foam will turn into continuation stoma structure easily.

[0034]

The 3rd process is a process of removing the moisture in the silicone foam of a damp or wet condition, and obtaining silicone foam. The dryer etc. which are usually used are used for removal of moisture. 100-180 ** of curing temperature is usually 120 ** - 160 ** preferably.

[0035]

Silicone foam will be obtained if the 3rd process is performed. A pore diameter is small and the pore diameter of this silicone foam is abbreviated homogeneity. the density of this silicone foam -- usually -- 0.10 - 0.80 g/cm^2 -- it is 0.20-0.40g[/cm] ^{2} preferably. 5-100 micrometers of pitch diameters of a stoma are usually 10-50 micrometers preferably. The voidage of this silicone foam is usually 20 to 50% preferably 15 to 90%. Here, voidage means the value which **(ed) the whole void product with bulk volume.

[0036]

The silicone foam obtained by this invention can be used as shock absorbing material, thermal insulation, etc., for example.

[0037]

[Working example]

Although an working example is shown below, this invention is limited to these and is not interpreted.

[0038]

Working example 1

Alkenyl-group content organopolysiloxane (Shin-Etsu Chemical Co. Ltd. KE106) 100 weight section of viscosity 3500cSt at 25 **, After agitating water 300 weight section and one end carbinol modified silicone oil (Shin-Etsu Chemical Co. Ltd. X-22-176DX) 80 weight section of viscosity 130cSt at 25 ** for 15 minutes by a hybrid mixer (made by KEYENCE CORP.), Hydrogen organopolysiloxane (Shin-Etsu Chemical Co. Ltd. CAT-RG) 10 weight section of viscosity 500cSt at 25 ** was added, it agitated for 1 minute, and the liquefied W / O type emulsion hardening raw material in which organopolysiloxane is contained in an oil reservoir was obtained. The platinum group system catalyst of sufficient quantity to carry out the addition reaction of alkenyl-group content organopolysiloxane and the hydrogen organopolysiloxane in addition to alkenyl-group content organopolysiloxane is included in Shin-Etsu Chemical Co. Ltd. KE106. This emulsion hardening raw material was poured into the mold, at 70 **, it heats for 3 hours, the addition reaction was carried out, and it was made to harden. Then, the silicone foam of the acquired damp or wet condition was neglected in a 150 ** dryer for 2 hours, and silicone foam was obtained. Density is

[the pitch diameter of 0.39 g/cm^2 and a stoma] 15 micrometers, voidage was 60%, this silicone foam is independent stoma structure, and it was contracted [the volume change before and behind hardening is -5%, and] after hardening. Here, a volume change is **(ed) by the volume before hardening the value which lengthened the volume before hardening from the volume after hardening.
[0039]
Working example 2
Make the loadings of a platinum group system catalyst into one weight section, and the loadings of water are made into 330 weight sections, To one end carbinol modified silicone oil 80 weight section. Both-ends carbinol modified silicone oil (Shin-Etsu Chemical Co. Ltd. KF6003) 25 weight section [in / it replaces with and / 25 **] of viscosity 110cSt, and the side-chain polyether modified silicone oil of viscosity 150cSt at 25 ** (HLB: Shin-Etsu Chemical Co. Ltd. KF6015) 4) Except having used 25 weight sections, like the working example 1, the creamy W / O type emulsion hardening raw material was obtained, and silicone foam was obtained like the working example 1. Density is [the pitch diameter of 0.35 g/cm^2 and a stoma] 80 micrometers, voidage was 65%, this silicone foam is continuation stoma structure, and it was contracted [the volume change before and behind hardening is -3%, and] after hardening.
[0040]
Comparative example 1
Make the loadings of a platinum group system catalyst into one weight section, and the loadings of water are made into 330 weight sections, It is made to be the same as that of the working example 1 except having replaced with one end carbinol modified silicone oil 80 weight section, and having used side-chain polyether modified silicone oil (Shin-Etsu Chemical Co. Ltd. KF6011, HLB:12) 30 weight section of viscosity 130cSt at 25 **, The liquefied O / W type emulsion hardening raw material was obtained. This emulsion hardening raw material was poured into the mold like the working example 1, when it heated for 3 hours and was made to harden at 70 **, only organopolysiloxane in an emulsion hardening raw material hardened massive, and the silicone foam of the damp or wet condition was not obtained.
[0041]
[Effect of the Invention]
According to the manufacturing method of the silicone foam concerning this invention, a pore diameter is small and the pore diameter of the silicone foam obtained is abbreviated homogeneity. It excels in rigidity and adiathermancy.
According to this method, the volume change at the time of forming the silicone foam of a damp or wet condition from a W / O type emulsion hardening raw material at the 2nd process is small. For this reason, silicone foam desirable as shock absorbing material or thermal insulation can be easily manufactured with shaping with a mold.

[Translation done.]

TECHNICAL FIELD

[Field of the Invention]
This invention relates to silicone foam suitably used as shock absorbing material or thermal insulation, and a manufacturing method for the same.
[0002]

[Translation done.]

PRIOR ART

[Description of the Prior Art]
Conventionally, various methods are known as a manufacturing method of silicone foam. For example, the method of obtaining silicone foam by making it harden using silicone rubber of the kind in which it foams at the time of hardening, The method (JP,H7-122000,B) of making it foam by generating of the steam at the time of heating is known by using the aquosity emulsion containing the water and the viscous agent as alkenyl-group content organopolysiloxane, an emulsifier, and a foaming agent as a base.
[0003]

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention]
According to the manufacturing method of the silicone foam concerning this invention, a pore diameter is small and the pore diameter of the silicone foam obtained is abbreviated homogeneity. It excels in rigidity and adiathermancy.
According to this method, the volume change at the time of forming the silicone foam of a damp or wet condition from a W / O type emulsion hardening raw material at the 2nd process is small. For this reason, silicone foam desirable as shock absorbing material or thermal insulation can be easily manufactured with shaping with a mold.

[Translation done.]

TECHNICAL PROBLEM

[Problem to be solved by the invention]
However, in the method to which the above gases are made to foam, since the path of the stoma in silicone foam was as large as about hundreds-1000 micrometers, rigidity and adiathermancy became insufficient easily. In order to make it foam with a gas, the problem that it was large and shaping with a mold was difficult also had a volume change before and behind foam curing. In order to make it foam with a gas, there was a problem that dispersion in the size of a stoma was large and it was difficult to control in a uniform size.
[0004]
Therefore, the purpose of this invention is to provide the manufacturing method of the silicone foam which can be manufactured in the state where the size of a stoma is small, and a volume change is small before and after form forming the silicone foam which is excellent in rigidity and adiathermancy, and this silicone foam.
[0005]

[Translation done.]

MEANS

[Means for solving problem]
As a result of inquiring wholeheartedly, this invention persons in this actual condition Alkenyl-group content organopolysiloxane, The size of a stoma is small, when a W / O type emulsion hardening raw material including a surface-active agent, hydrogen organopolysiloxane, water, and a platinum group system catalyst is heated and the addition reaction of alkenyl-group content organopolysiloxane and hydrogen organopolysiloxane in an oil reservoir is carried out, Before and after form forming the silicone foam which is excellent in rigidity and adiathermancy, a volume change finds out that it can manufacture in the small state, and came to complete this invention.
[0006]
This invention Namely, alkenyl-group content organopolysiloxane 100 weight section, One to surface-active agent 300 weight section, 0.1 to hydrogen organopolysiloxane 50 weight section, The 1st process of obtaining a W / O type emulsion hardening raw material including 20 to water 1500 weight section, and a platinum group system catalyst, Heat this W / O type emulsion hardening raw material, and the addition reaction of said alkenyl-group content organopolysiloxane and said hydrogen organopolysiloxane in an oil reservoir is carried out, The manufacturing method of silicone foam including the 3rd process of removing the moisture in the silicone foam of the 2nd process of obtaining the silicone foam of a damp or wet condition, and this damp or wet condition, and obtaining silicone foam is provided.
[0007]
As for this invention, density provides silicone foam, wherein 0.10-0.80g[/cm] ^{3} and an average pore diameter are 5-100 micrometers.
[0008]
[Mode for carrying out the invention]
The 1st process is a process of obtaining a W / O type emulsion hardening raw material including alkenyl-group content organopolysiloxane, a surface-active agent, hydrogen organopolysiloxane, water, and a platinum group system catalyst.
[0009]
The alkenyl-group content organopolysiloxane used by this invention is the following average composition formula (1).
$R^1{}_nSiO_{(4-n)/2}$ (1)
(-- substitution that the inside of a formula and R^1 are the same, or of a different kind or an unsubstituted monovalent hydrocarbon group, and n -- 1.95-2.08 -- it is a positive number of 1.98-2.02 preferably.) -- it is organopolysiloxane shown and has the alkenyl group combined with an average of two or more silicon atoms in the molecule.
[0010]
R^1 is the carbon numbers 1-12 combined with the silicon atom especially the substitution of 1-8, or

an unsubstituted monovalent hydrocarbon group here, For example, a methyl group, an ethyl group, a propyl group, an isopropyl group, a butyl group, An isobutyl group, a tert-butyl group, a pentyl group, a neopentyl group, Alkyl groups, such as a hexyl group, a heptyl group, an octyl group, a nonyl group, a decyl group, and dodecyl, Cycloalkyl groups, such as a cyclopentylic group, a cyclohexyl group, and a cycloheptyl group, A vinyl group, an allyl group, a propenyl group, an isopropenyl group, a butenyl group, Alkenyl groups, such as an isobutenyl group, a hexenyl group, and a cyclohexenyl group, Aryl groups, such as a phenyl group, a tolyl group, a xylyl group, a naphthyl group, and a biphenyl group, The chloromethyl group by which some or all of the hydrogen atom in aralkyl groups, such as benzyl, a phenylethyl group, a phenylpropyl group, and a methylbenzyl group, or these hydrocarbon groups was replaced by halogen atoms, cyano groups, etc., such as F, Cl, and Br, 2-bromoethyl group, a 3,3,3-trifluoropropyl group, 3-chloropropyl group, a cyanoethyl group, etc. are mentioned.

[0011]

In this case, at least an average of two in the substitution shown by the above-mentioned R^1 or an unsubstituted monovalent hydrocarbon group are an alkenyl group, and, as for especially the quantity of an alkenyl group, 0.001-0.1 mol is preferred 0.0001-1 mol in the alkenyl-group content organopolysiloxane 100g. It may combine with the silicon atom of molecular chain terminals, or may combine with the silicon atom in the middle of a chain, and an alkenyl group may exist in both.

[0012]

As for n, it is preferred among the above-mentioned formula (1) 1.95-2.08, and that it is a positive number of 1.98-2.02 preferably, and the molecular structure of this alkenyl-group content organopolysiloxane is straight chain shape which consists of a repetition of JIORUGANO siloxane units. Although it is preferred that it is what has an alkenyl group in chain both ends at least, it may have the branched state structure which includes $R^1SiO_{3/2}$ unit, and $SiO_{4/2}$ unit in a part. As for this alkenyl-group content organopolysiloxane, it is preferred that those molecular chain terminals are blocked by bird organosilyl groups, such as trivinylsilyl, methyldi vinylsilyl, dimethylvinylsilyl, or a trimethylsilyl group.

[0013]

It is usually 25 or more cSt at 25 **, and since emulsion-izing according that it is 250 - 10,000cSt still more preferably to churning is preferably easy for the viscosity of this alkenyl-group content organopolysiloxane 25 to 500,000 cSt, it is preferred.

[0014]

As a surface-active agent used by this invention, hydrophilic radical denaturation organopolysiloxane is mentioned, for example. Here, hydrophilic radical denaturation organopolysiloxane means the organopolysiloxane which has hydrophilic radicals, such as a hydroxyl group and an organic group which has an ether bond. Since alkenyl-group content organopolysiloxane and hydrogen organopolysiloxane which are contained in an oil reservoir in this invention as the hydrophobic part of a surface-active agent is organopolysiloxane, and compatibility are good, it is desirable. At least one sort chosen from the group which consists of carbinol modified silicone oil, polyether modified silicone oil, epoxy modified silicone oil, and carboxyl modified silicone oil as such hydrophilic radical denaturation organopolysiloxane, for example is mentioned.

[0015]

As for hydrophilic radical denaturation organopolysiloxane, if only the both ends or one end of a molecule denaturalizes by a hydrophilic group, in order that hydrophilic radical denaturation organopolysiloxane may show the dispersion effect of the waterdrop by steric exclusion, the form of independent stoma structure will become is easy to be obtained. On the other hand, if the side chain of a molecule denaturalizes by a hydrophilic group, hydrophilic radical denaturation organopolysiloxane has the weak electrostatic repulsion between waterdrop, and since waterdrop adjoins and exists in an emulsion, the form of continuation stoma structure will become is easy to be obtained. Therefore, what is necessary is just to choose the kind of hydrophilic radical

denaturation organopolysiloxane suitably according to the stoma structure expected to the silicone foam to manufacture.
[0016]
although HLB of a surface-active agent is not what is limited especially since a W / O type emulsion hardening raw material should just be obtained as a result in this invention -- usually -- 0-6 -- it is 0-4 preferably.
[0017]
The viscosity at 25 ** of a surface-active agent is usually 10 - 1000cSt preferably ten to 30000 cSt. When viscosity is in this within the limits, since emulsion-izing by churning is easy, it is desirable.
[0018]
The hydrogen organopolysiloxane used by this invention, It is organopolysiloxane which has at least two SiH groups (namely, hydrogen atom combined with the silicon atom) in one molecule, Although it may be any of straight chain shape, annular, branched state, and three-dimensional network structure and the publicly known ORGANO hydrogen polysiloxane can be used as a hardening agent (cross linking agent) of an addition reaction hardening type silicone rubber composition, it is usually the following average composition formula (2).
$R^2_aH_bSiO_{(4-a-b)/2}$ (2)
the inside of a formula and R^2 are the same as that of the above-mentioned R^1 -- desirable -- the carbon numbers 1-12 -- especially -- the alkyl group of 1-8. It is an alkenyl group, an aryl group, an aralkyl group, and unsubstituted or the substitution monovalent hydrocarbon group of these halogenation objects, and what does not contain aliphatic unsaturated bonds is preferred, and a methyl group, a phenyl group, and a 3,3,3-trifluoropropyl group are preferred especially. a and b are $0.802<=a+b<=3$ and a positive number which fills $1.01 <=a+b<=2.5$ with $1<=a<=2$ and $0.01<=b<=1$ preferably in $0.8<=a<=2.2$ and $0.002<=b<=1$. What is shown can be used.
[0019]
Although it has preferably the three or more above-mentioned SiH groups in [at least two] one molecule, this may be in molecular chain terminals, or there may be in the middle of a chain. Since emulsion-izing according that the viscosity at 25 ** is especially 1 - 1,000cSt one to 10,000 cSt to churning is easy for the ORGANO hydrogen polysiloxane, it is preferred. As for especially the ORGANO hydrogen polysiloxane, it is preferred that the 2-500 number of degrees of polymerization, i.e., the silicon atom in one molecule, is 4-200.
[0020]
The platinum group system catalyst used by this invention is a catalyst for carrying out the addition reaction of the silicon atom absorbed water matter atom in hydrogen organopolysiloxane to the alkenyl group of alkenyl-group content organopolysiloxane. As a platinum group system catalyst, there are the metal simple substance and compound of a platinum group, and a publicly known thing can be conventionally used for this. For example, the particle-like platinum metal made to adsorb on platinum black, silica, alumina, or a carrier like silica gel, A complex with platinic chloride, chloroplatinic acid, and chloroplatinic acid 6 monohydrate, an olefin, or divinyl dimethylpolysiloxane, the alcohol solution of chloroplatinic acid 6 monohydrate, a palladium catalyst, a rhodium catalyst, etc. are mentioned.
[0021]
In the 1st process, the above-mentioned alkenyl-group content organopolysiloxane, a surface-active agent, hydrogen organopolysiloxane, water, and a platinum group system catalyst are mixed, and the W / O type emulsion hardening raw material containing these is obtained. In this invention, say a W / O type emulsion hardening raw material, and the raw material of the heat cure of the 2nd process specifically, It is a mixture including alkenyl-group content organopolysiloxane, a surface-active agent, hydrogen organopolysiloxane, water, and a platinum group system catalyst, and what presents

a W / O type emulsion is said.

[0022]

It is not limited, and may dissolve, for example in a suitable order for water, and especially mixed sequence forewords, such as alkenyl-group content organopolysiloxane in the case of preparation of a W / O type emulsion hardening raw material, may mix these simultaneously. However, as for hydrogen organopolysiloxane, since it is easy to hydrolyze if water is contacted, it is preferred to contact hydrogen organopolysiloxane and water just before the 2nd process.

[0023]

Thus, as a method of making it contacting just before the 2nd process, hydrogen organopolysiloxane and water, In the 1st process, first specifically Alkenyl-group content organopolysiloxane, The 1st (a) process of mixing a surface-active agent, water, and a platinum group system catalyst, and obtaining a W / O type emulsion reserve raw material is performed, Next, the method of performing the 1st (b) process of adding hydrogen organopolysiloxane in this W / O type emulsion reserve raw material, and obtaining a W / O type emulsion hardening raw material is mentioned. In this invention, a W / O type emulsion reserve raw material is a mixture including alkenyl-group content organopolysiloxane, a surface-active agent, water, and a platinum group system catalyst, and what presents a W / O type emulsion is said.

[0024]

As a mixing method in the case of preparation of a W / O type emulsion hardening raw material or a W / O type emulsion reserve raw material, Although it may carry out using a common agitator, since generation of a W / O type emulsion hardening raw material or a W / O type emulsion reserve raw material will be promptly performed if emulsion machines, such as a homogenizer, are used, it is desirable.

[0025]

The loadings of the surface-active agent in a W / O type emulsion hardening raw material are usually five to 100 weight section preferably one to 300 weight section to alkenyl-group content organopolysiloxane 100 weight section. When the loadings of a surface-active agent are in this within the limits, since it is easy to obtain a W / O type emulsion, it is desirable.

[0026]

The loadings of hydrogen organopolysiloxane in a W / O type emulsion hardening raw material are usually 0.1 to 50 weight section to alkenyl-group content organopolysiloxane 100 weight section. When the loadings of hydrogen organopolysiloxane are in this within the limits, since the mechanical strength of silicone foam and heat resistance which are obtained become high enough, it is desirable.

[0027]

In a W / O type emulsion hardening raw material, the rate of a compounding ratio of alkenyl-group content organopolysiloxane and hydrogen organopolysiloxane, The rate of the hydrogen atom combined with the silicon atom in hydrogen organopolysiloxane to one alkenyl group combined with the silicon atom in alkenyl-group content organopolysiloxane is usually 0.5-10 pieces, and is 1-4 pieces preferably. When the rate of a compounding ratio is in this within the limits, since the mechanical strength of silicone foam and heat resistance which are obtained become high enough, it is desirable.

[0028]

The loadings of the water in a W / O type emulsion hardening raw material are usually 100 to 300 weight section preferably 20 to 1500 weight section to alkenyl-group content organopolysiloxane 100 weight section. When the loadings of water are in this within the limits, since it is easy to obtain a W / O type emulsion and the voidage of the silicone foam obtained becomes large easily, it is desirable. Although it is it easy to obtain a W / O type emulsion that the loadings of water are less than 100 weight sections, since form becomes hard easily when voidage becomes small, it is not desirable. If the loadings of water exceed 300 weight sections, although voidage becomes large and

can produce soft form, since it is difficult to get, it is not desirable in a W / O type emulsion.
[0029]
Although a publicly known quantity of the grade which can promote an addition reaction may be sufficient as the loadings of the platinum group system catalyst over a W / O type emulsion hardening raw material, the concentration after adding in a W / O type emulsion hardening raw material is the quantity converted into the amount of platinum metals, and it is made to usually be set to 0.5-1000 ppm, for example. When the loadings of a platinum group system catalyst are in this within the limits, an addition reaction is usually fully promoted, and since it is economical, it is desirable.
[0030]
If the 1st process is performed, the liquefied or creamy W / O type emulsion hardening raw material which has alkenyl-group content organopolysiloxane, hydrogen organopolysiloxane, and a platinum group system catalyst in an oil reservoir will generate. Water is contained in the water layer distributed in an oil reservoir, and the above-mentioned surface-active agent exists in an interface. the -- the liquefied or creamy W / O type emulsion hardening raw material which has alkenyl-group content organopolysiloxane and a platinum group system catalyst in an oil reservoir generates the W / O type emulsion reserve raw material obtained after 1(a) process.
[0031]
The 2nd process is a process of heating the above-mentioned W / O type emulsion hardening raw material, stiffening said alkenyl-group content organopolysiloxane and said hydrogen organopolysiloxane in an oil reservoir, and obtaining the silicone foam of a damp or wet condition.
[0032]
50-100 ** of cooking temperature is usually 60-80 ** preferably. When cooking temperature is in this within the limits, since volatilization of water before an oil reservoir hardens can be controlled, it is desirable. Since the stoma generated in form when water boils will become big and rough if 100 ** is exceeded, cooking temperature is not preferred. It is not desirable in order to take a long time for an oil reservoir to harden that cooking temperature is less than 50 **. Cooking time is usually 0.5 to 3 hours preferably for 0.5 to 10 hours.
[0033]
If the 2nd process is performed, the silicone foam of a damp or wet condition will be obtained. In order that alkenyl-group content organopolysiloxane and hydrogen organopolysiloxane in the oil reservoir of a W / O type emulsion hardening raw material may carry out the addition reaction of the silicone foam of this damp or wet condition as it is and may harden it, it originates in a water layer -- abbreviated -- the silicone foam which has a stoma of a uniform size is obtained. If the hydrophilic radical denaturation organopolysiloxane in which only the both ends or one end of the molecule denaturalized by the hydrophilic group is used for silicone foam as a surface-active agent as mentioned above, the stoma structure of silicone foam will turn into independent stoma structure easily. If the side chain of a molecule uses the hydrophilic radical denaturation organopolysiloxane which denaturalized by the hydrophilic group, the stoma structure of silicone foam will turn into continuation stoma structure easily.
[0034]
The 3rd process is a process of removing the moisture in the silicone foam of a damp or wet condition, and obtaining silicone foam. The dryer etc. which are usually used are used for removal of moisture. 100-180 ** of curing temperature is usually 120 ** - 160 ** preferably.
[0035]
Silicone foam will be obtained if the 3rd process is performed. A pore diameter is small and the pore diameter of this silicone foam is abbreviated homogeneity. the density of this silicone foam -- usually -- 0.10 - 0.80 g/cm^2 -- it is 0.20-0.40g[/cm] ^{2} preferably. 5-100 micrometers of pitch diameters of a stoma are usually 10-50 micrometers preferably. The voidage of this silicone foam is usually 20 to 50% preferably 15 to 90%. Here, voidage means the value which **(ed) the whole void

product with bulk volume.
[0036]
The silicone foam obtained by this invention can be used as shock absorbing material, thermal insulation, etc., for example.
[0037]

[Translation done.]

EXAMPLE

[Working example]
Although an working example is shown below, this invention is limited to these and is not interpreted.
[0038]
Working example 1
Alkenyl-group content organopolysiloxane (Shin-Etsu Chemical Co. Ltd. KE106) 100 weight section of viscosity 3500cSt at 25 **, After agitating water 300 weight section and one end carbinol modified silicone oil (Shin-Etsu Chemical Co. Ltd. X-22-176DX) 80 weight section of viscosity 130cSt at 25 ** for 15 minutes by a hybrid mixer (made by KEYENCE CORP.), Hydrogen organopolysiloxane (Shin-Etsu Chemical Co. Ltd. CAT-RG) 10 weight section of viscosity 500cSt at 25 ** was added, it agitated for 1 minute, and the liquefied W / O type emulsion hardening raw material in which organopolysiloxane is contained in an oil reservoir was obtained. The platinum group system catalyst of sufficient quantity to carry out the addition reaction of alkenyl-group content organopolysiloxane and the hydrogen organopolysiloxane in addition to alkenyl-group content organopolysiloxane is included in Shin-Etsu Chemical Co. Ltd. KE106. This emulsion hardening raw material was poured into the mold, at 70 **, it heats for 3 hours, the addition reaction was carried out, and it was made to harden. Then, the silicone foam of the acquired damp or wet condition was neglected in a 150 ** dryer for 2 hours, and silicone foam was obtained. Density is [the pitch diameter of 0.39 g/cm^2 and a stoma] 15 micrometers, voidage was 60%, this silicone foam is independent stoma structure, and it was contracted [the volume change before and behind hardening is -5%, and] after hardening. Here, a volume change is **(ed) by the volume before hardening the value which lengthened the volume before hardening from the volume after hardening.
[0039]
Working example 2
Make the loadings of a platinum group system catalyst into one weight section, and the loadings of water are made into 330 weight sections, To one end carbinol modified silicone oil 80 weight section. Both-ends carbinol modified silicone oil (Shin-Etsu Chemical Co. Ltd. KF6003) 25 weight section [in / it replaces with and / 25 **] of viscosity 110cSt, and the side-chain polyether modified silicone oil of viscosity 150cSt at 25 ** (HLB: Shin-Etsu Chemical Co. Ltd. KF6015) 4) Except having used 25 weight sections, like the working example 1, the creamy W / O type emulsion hardening raw material was obtained, and silicone foam was obtained like the working example 1. Density is [the pitch diameter of 0.35 g/cm^2 and a stoma] 80 micrometers, voidage was 65%, this silicone foam is continuation stoma structure, and it was contracted [the volume change before and behind hardening is -3%, and] after hardening.
[0040]
Comparative example 1
Make the loadings of a platinum group system catalyst into one weight section, and the loadings of

water are made into 330 weight sections, It is made to be the same as that of the working example 1 except having replaced with one end carbinol modified silicone oil 80 weight section, and having used side-chain polyether modified silicone oil (Shin-Etsu Chemical Co. Ltd. KF6011, HLB:12) 30 weight section of viscosity 130cSt at 25 **, The liquefied O / W type emulsion hardening raw material was obtained. This emulsion hardening raw material was poured into the mold like the working example 1, when it heated for 3 hours and was made to harden at 70 **, only organopolysiloxane in an emulsion hardening raw material hardened massive, and the silicone foam of the damp or wet condition was not obtained.
[0041]

[Translation done.]

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(54)【発明の名称】シリコーンフォーム及びその製造方法

(57)【要約】
【課題】気孔の大きさが小さく、剛性及び断熱性に優れるシリコーンフォーム及び該シリコーンフォームをフォーム形成の前後において体積変化が小さい状態で製造できるシリコーンフォームの製造方法を提供すること。
【解決手段】アルケニル基含有オルガノポリシロキサン１００重量部、界面活性剤１～３００重量部、ハイドロジェンオルガノポリシロキサン０．１～５０重量部、水２０～１５００重量部及び白金族系触媒を含む油中水滴型エマルション硬化原料を得る第１工程、該油中水滴型エマルション硬化原料を加熱して油層中の前記アルケニル基含有オルガノポリシロキサンと前記ハイドロジェンオルガノポリシロキサンとを付加反応させ、湿潤状態のシリコーンフォームを得る第２工程及び該湿潤状態のシリコーンフォーム中の水分を除去してシリコーンフォームを得る第３工程を含むシリコーンフォームの製造方法。
【選択図】　なし

【特許請求の範囲】
【請求項１】
アルケニル基含有オルガノポリシロキサン１００重量部、界面活性剤１～３００重量部、ハイドロジェンオルガノポリシロキサン０．１～５０重量部、水２０～１５００重量部及び白金族系触媒を含む油中水滴型エマルション硬化原料を得る第１工程、該油中水滴型エマルション硬化原料を加熱して油層中の前記アルケニル基含有オルガノポリシロキサンと前記ハイドロジェンオルガノポリシロキサンとを付加反応させ、湿潤状態のシリコーンフォームを得る第２工程及び該湿潤状態のシリコーンフォーム中の水分を除去してシリコーンフォームを得る第３工程を含むことを特徴とするシリコーンフォームの製造方法。
【請求項２】
前記第１工程が、アルケニル基含有オルガノポリシロキサン１００重量部、界面活性剤１～３００重量部、水２０～１５００重量部及び白金族系触媒を含む油中水滴型エマルション予備原料を得る第１（ａ）工程及び該油中水滴型エマルション予備原料にハイドロジェンオルガノポリシロキサン０．１～５０重量部を添加して油中水滴型エマルション硬化原料を得る第１（ｂ）工程からなることを特徴とする請求項１記載のシリコーンフォームの製造方法。
【請求項３】
前記界面活性剤が、親水性基変性オルガノポリシロキサンであることを特徴とする請求項１又は２記載のシリコーンフォームの製造方法。
【請求項４】
前記親水性基変性オルガノポリシロキサンが、カルビノール変性シリコーンオイル、ポリエーテル変性シリコーンオイル、エポキシ変性シリコーンオイル及びカルボキシル変性シリコーンオイルからなる群より選択される少なくとも１種のシリコーンオイルであることを特徴とする請求項３記載のシリコーンフォームの製造方法。
【請求項５】
密度が０．１０～０．８０g/cm^3、平均気孔径が５～１００μｍであることを特徴とするシリコーンフォーム。
【発明の詳細な説明】
【０００１】
【発明の属する技術分野】
本発明は、緩衝材や断熱材として好適に用いられるシリコーンフォーム及びその製造方法に関するものである。
【０００２】
【従来の技術】
従来、シリコーンフォームの製造方法として種々の方法が知られている。例えば、硬化時に発泡する種類のシリコーンゴムを用いて硬化させることによりシリコーンフォームを得る方法や、アルケニル基含有オルガノポリシロキサン、乳化剤、発泡剤としての水及び粘剤を含有する水性エマルションをベースとして、加熱時の水蒸気の発生により発泡させる方法（特公平７－１２２０００号公報）が知られている。
【０００３】
【発明が解決しようとする課題】
しかしながら、上記のような気体を発泡させる方法では、シリコーンフォーム中の気孔の径が数百～１０００μｍ程度と大きいため、剛性や断熱性が不充分になり易かった。また、気体によって発泡させるため、発泡硬化前後の体積変化が大きく、型による成形が困難であるという問題もあった。さらに、気体によって発泡させるため、気孔の大きさのばらつきが大きく、均一な大きさに制御することが困難であるという問題があった。
【０００４】
従って、本発明の目的は、気孔の大きさが小さく、剛性及び断熱性に優れるシリコーンフォーム及び該シリコーンフォームをフォーム形成の前後において体積変化が小さい状態で製造できるシリコーンフォームの製造方法を提供することにある。

【0005】

【課題を解決するための手段】

かかる実情において、本発明者らは鋭意検討を行った結果、アルケニル基含有オルガノポリシロキサン、界面活性剤、ハイドロジェンオルガノポリシロキサン、水及び白金族系触媒を含む油中水滴型エマルション硬化原料を加熱して油層中のアルケニル基含有オルガノポリシロキサンとハイドロジェンオルガノポリシロキサンとを付加反応させると、気孔の大きさが小さく、剛性及び断熱性に優れるシリコーンフォームをフォーム形成の前後において体積変化が小さい状態で製造できることを見出し、本発明を完成するに至った。

【0006】

すなわち、本発明は、アルケニル基含有オルガノポリシロキサン100重量部、界面活性剤1～300重量部、ハイドロジェンオルガノポリシロキサン0．1～50重量部、水20～1500重量部及び白金族系触媒を含む油中水滴型エマルション硬化原料を得る第1工程、該油中水滴型エマルション硬化原料を加熱して油層中の前記アルケニル基含有オルガノポリシロキサンと前記ハイドロジェンオルガノポリシロキサンとを付加反応させ、湿潤状態のシリコーンフォームを得る第2工程及び該湿潤状態のシリコーンフォーム中の水分を除去してシリコーンフォームを得る第3工程を含むことを特徴とするシリコーンフォームの製造方法を提供するものである。

【0007】

また、本発明は、密度が0．10～0．80g/cm^3、平均気孔径が5～100μmであることを特徴とするシリコーンフォームを提供するものである。

【0008】

【発明の実施の形態】

第1工程は、アルケニル基含有オルガノポリシロキサン、界面活性剤、ハイドロジェンオルガノポリシロキサン、水及び白金族系触媒を含む油中水滴型エマルション硬化原料を得る工程である。

【0009】

本発明で用いられるアルケニル基含有オルガノポリシロキサンは、下記平均組成式（1）

$$R^1{}_n SiO_{(4-n)/2} \qquad (1)$$

（式中、R^1は同一又は異種の置換又は非置換一価炭化水素基、nは1．95～2．08、好ましくは1．98～2．02の正数である。）で示されるオルガノポリシロキサンであって、分子中に平均2個以上の珪素原子に結合したアルケニル基を有するものである。

【0010】

ここで、R^1は、珪素原子に結合した炭素数1～12、特に1～8の置換又は非置換の一価炭化水素基であり、例えばメチル基、エチル基、プロピル基、イソプロピル基、ブチル基、イソブチル基、tert－ブチル基、ペンチル基、ネオペンチル基、ヘキシル基、ヘプチル基、オクチル基、ノニル基、デシル基、ドデシル基等のアルキル基、シクロペンチル基、シクロヘキシル基、シクロヘプチル基等のシクロアルキル基、ビニル基、アリル基、プロペニル基、イソプロペニル基、ブテニル基、イソブテニル基、ヘキセニル基、シクロヘキセニル基等のアルケニル基、フェニル基、トリル基、キシリル基、ナフチル基、ビフェニル基等のアリール基、ベンジル基、フェニルエチル基、フェニルプロピル基、メチルベンジル基等のアラルキル基やこれらの炭化水素基中の水素原子の一部又は全部がF，Cl，Br等のハロゲン原子やシアノ基などで置換されたクロロメチル基、2－ブロモエチル基、3，3，3－トリフルオロプロピル基、3－クロロプロピル基、シアノエチル基等が挙げられる。

【0011】

この場合、上記R^1で示される置換又は非置換の一価炭化水素基のうち、少なくとも平均2個はアルケニル基であり、アルケニル基の量は、アルケニル基含有オルガノポリシロキサン100g中に0．0001～1モル、特に0．001～0．1モルが好ましい。なお、アルケニル基は分子鎖末端の珪素原子に結合していても、分子鎖途中のケイ素原子に結合していてもよく、両者に存在してもよい。

【００１２】
また、上記式（１）中、ｎは１．９５～２．０８、好ましくは１．９８～２．０２の正数であり、このアルケニル基含有オルガノポリシロキサンの分子構造はジオルガノシロキサン単位の繰り返しからなる直鎖状であることが好ましい。また少なくとも分子鎖両末端にアルケニル基を有するものであることが好ましいが、一部分に$R^1SiO_{3/2}$単位や$SiO_{4/2}$単位を含む分岐状構造を有していてもよい。なお、このアルケニル基含有オルガノポリシロキサンは、その分子鎖末端がトリビニルシリル、メチルジビニルシリル、ジメチルビニルシリル又はトリメチルシリル基などのトリオルガノシリル基で封鎖されていることが好ましい。

【００１３】
このアルケニル基含有オルガノポリシロキサンの粘度は、２５℃で通常２５ｃＳｔ以上であり、好ましくは２５～５００，０００ｃＳｔ、さらに好ましくは２５０～１０，０００ｃＳｔであると、攪　によるエマルション化が容易であるため好ましい。

【００１４】
本発明で用いられる界面活性剤としては、例えば、親水性基変性オルガノポリシロキサンが挙げられる。ここで、親水性基変性オルガノポリシロキサンとは、水酸基、エーテル結合を有する有機基等の親水性基を有しているオルガノポリシロキサンをいう。本発明では、界面活性剤の疎水性部分がオルガノポリシロキサンであると、油層に含まれるアルケニル基含有オルガノポリシロキサン及びハイドロジェンオルガノポリシロキサンと相溶性が良いため好ましい。このような親水性基変性オルガノポリシロキサンとしては、例えば、カルビノール変性シリコーンオイル、ポリエーテル変性シリコーンオイル、エポキシ変性シリコーンオイル及びカルボキシル変性シリコーンオイルからなる群より選択される少なくとも１種が挙げられる。

【００１５】
なお、親水性基変性オルガノポリシロキサンは分子の両末端又は片末端のみが親水基で変性されたものであると、親水性基変性オルガノポリシロキサンが立体障害による水滴の分散効果を示すため独立気孔構造のフォームが得られ易くなる。一方、親水性基変性オルガノポリシロキサンは分子の側鎖が親水基で変性されたものであると、水滴間の静電反発力が弱く、エマルション中で水滴が隣接して存在するため連続気孔構造のフォームが得られ易くなる。従って、親水性基変性オルガノポリシロキサンの種類は、製造するシリコーンフォームに望む気孔構造に合わせて適宜選択すればよい。

【００１６】
本発明において、界面活性剤のＨＬＢは、結果として油中水滴型エマルション硬化原料が得られればよいため特に限定されるものではないが、通常０～６、好ましくは０～４である。

【００１７】
また、界面活性剤の２５℃における粘度は、通常１０～３００００ｃＳｔ、好ましくは１０～１０００ｃＳｔである。粘度が該範囲内にあると、攪　によるエマルション化が容易であるため好ましい。

【００１８】
本発明で用いられるハイドロジェンオルガノポリシロキサンは、１分子中に少なくとも２個のＳｉＨ基（即ち、ケイ素原子に結合した水素原子）を有するオルガノポリシロキサンであり、直鎖状、環状、分岐状、三次元網状構造のいずれであってもよく、付加反応硬化型シリコーンゴム組成物の硬化剤（架橋剤）として公知のオルガノハイドロジェンポリシロキサンを用いることができるが、通常、下記平均組成式（２）

$$R^2_aH_bSiO_{(4-a-b)/2} \qquad (2)$$

（式中、R^2は上記R^1と同様の好ましくは炭素数１～１２、特に１～８のアルキル基、アルケニル基、アリール基、アラルキル基や、これらのハロゲン置換体などの非置換又は置換一価炭化水素基であり、脂肪族不飽和結合を含有しないものが好ましく、特に、メチル基、フェニル基、３，３，３－トリフルオロプロピル基が好ましい。a，bは０．８≦

a≦２．２、０．００２≦b≦１で０．８０２≦a＋b≦３、好ましくは１≦a≦２、０．０１≦b≦１で１．０１≦a＋b≦２．５を満たす正数である。）で示されるものを用いることができる。

【００１９】

上記ＳｉＨ基は１分子中に少なくとも２個、好ましくは３個以上有するが、これは分子鎖末端にあっても、分子鎖の途中にあってもよい。また、オルガノハイドロジェンポリシロキサンは、２５℃における粘度が１～１０，０００ｃＳｔ、特に１～１，０００ｃＳｔであると、攪　によるエマルション化が容易であるため好ましい。またオルガノハイドロジェンポリシロキサンは、重合度、すなわち、１分子中のケイ素原子の数が２～５００個、特に４～２００個であることが好ましい。

【００２０】

本発明で用いられる白金族系触媒は、アルケニル基含有オルガノポリシロキサンのアルケニル基とハイドロジェンオルガノポリシロキサン中のケイ素原子結合水素原子を付加反応させるための触媒である。白金族系触媒としては白金族の金属単体とその化合物があり、これには従来公知のものを用いることができる。例えば、白金黒、シリカ、アルミナ又はシリカゲルのような担体上に吸着させた微粒子状白金金属、塩化第二白金、塩化白金酸、塩化白金酸６水塩とオレフィン又はジビニルジメチルポリシロキサンとの錯体、塩化白金酸６水塩のアルコール溶液、パラジウム触媒、ロジウム触媒等が挙げられる。

【００２１】

第１工程では、上記アルケニル基含有オルガノポリシロキサン、界面活性剤、ハイドロジェンオルガノポリシロキサン、水及び白金族系触媒を混合して、これらを含む油中水滴型エマルション硬化原料を得る。本発明において、油中水滴型エマルション硬化原料とは第２工程の加熱硬化の原料をいい、具体的には、アルケニル基含有オルガノポリシロキサン、界面活性剤、ハイドロジェンオルガノポリシロキサン、水及び白金族系触媒を含む混合物であって、油中水滴型エマルションを呈するものをいう。

【００２２】

油中水滴型エマルション硬化原料の調製の際におけるアルケニル基含有オルガノポリシロキサン等の混合順序は、特に限定されるものでなく、例えば水に適当な順序で溶解していってもよいし、これらを同時に混合してもよい。ただし、ハイドロジェンオルガノポリシロキサンは水と接触すると加水分解し易いため、ハイドロジェンオルガノポリシロキサンと水とは、第２工程の直前に接触させることが好ましい。

【００２３】

このようにハイドロジェンオルガノポリシロキサンと水とを第２工程の直前に接触させる方法としては、具体的には、第１工程において、まず、アルケニル基含有オルガノポリシロキサン、界面活性剤、水及び白金族系触媒を混合して油中水滴型エマルション予備原料を得る第１（a）工程を行い、次に、該油中水滴型エマルション予備原料にハイドロジェンオルガノポリシロキサンを添加して油中水滴型エマルション硬化原料を得る第１（b）工程を行う方法が挙げられる。なお、本発明において、油中水滴型エマルション予備原料とは、アルケニル基含有オルガノポリシロキサン、界面活性剤、水及び白金族系触媒を含む混合物であって、油中水滴型エマルションを呈するものをいう。

【００２４】

油中水滴型エマルション硬化原料又は油中水滴型エマルション予備原料の調製の際における混合方法としては、一般的な攪　機を用いて行ってもよいが、ホモジナイザ等の乳化機を用いると油中水滴型エマルション硬化原料又は油中水滴型エマルション予備原料の生成が迅速に行われるため好ましい。

【００２５】

油中水滴型エマルション硬化原料における界面活性剤の配合量は、アルケニル基含有オルガノポリシロキサン１００重量部に対し、通常１～３００重量部、好ましくは５～１００重量部である。界面活性剤の配合量が該範囲内にあると、油中水滴型エマルションを得易いため好ましい。

【００２６】
油中水滴型エマルション硬化原料におけるハイドロジェンオルガノポリシロキサンの配合量は、アルケニル基含有オルガノポリシロキサン１００重量部に対し、通常０．１～５０重量部である。ハイドロジェンオルガノポリシロキサンの配合量が該範囲内にあると、得られるシリコーンフォームの機械的強度及び耐熱性が十分に高くなるため好ましい。
【００２７】
また、油中水滴型エマルション硬化原料において、アルケニル基含有オルガノポリシロキサンとハイドロジェンオルガノポリシロキサンとの配合比率は、アルケニル基含有オルガノポリシロキサン中のケイ素原子に結合したアルケニル基１個に対して、ハイドロジェンオルガノポリシロキサン中のケイ素原子に結合した水素原子の割合が通常０．５～１０個であり、好ましくは１～４個である。配合比率が該範囲内にあると、得られるシリコーンフォームの機械的強度及び耐熱性が十分に高くなるため好ましい。
【００２８】
油中水滴型エマルション硬化原料における水の配合量は、アルケニル基含有オルガノポリシロキサン１００重量部に対し、通常２０～１５００重量部、好ましくは１００～３００重量部である。水の配合量が該範囲内にあると、油中水滴型エマルションを得易く、また、得られるシリコーンフォームの空隙率が大きくなり易いため好ましい。なお、水の配合量が１００重量部未満であると、油中水滴型エマルションを得易いけれども、空隙率が小さくなることによりフォームが硬くなり易いため好ましくない。また、水の配合量が３００重量部を越えると、空隙率が大きくなりソフトなフォームを作製できるけれども、油中水滴型エマルションを得難いため好ましくない。
【００２９】
油中水滴型エマルション硬化原料に対する白金族系触媒の配合量は、付加反応を促進できる程度の公知の量でよいが、例えば、油中水滴型エマルション硬化原料に添加した後の濃度が、白金族金属量に換算した量で、通常０．５～１０００ＰＰｍになるようにする。白金族系触媒の配合量が該範囲内にあると、通常付加反応が十分に促進され、且つ、経済的であるため好ましい。
【００３０】
第１工程を行うと、アルケニル基含有オルガノポリシロキサン、ハイドロジェンオルガノポリシロキサン及び白金族系触媒が油層にある液状又はクリーム状の油中水滴型エマルション硬化原料が生成する。油層中に分散する水層には水が含まれ、界面には上記界面活性剤が存在する。なお、第１（α）工程後に得られる油中水滴型エマルション予備原料は、アルケニル基含有オルガノポリシロキサン及び白金族系触媒が油層にある液状又はクリーム状の油中水滴型エマルション硬化原料が生成する。
【００３１】
第２工程は、上記油中水滴型エマルション硬化原料を加熱して油層中の前記アルケニル基含有オルガノポリシロキサン及び前記ハイドロジェンオルガノポリシロキサンを硬化させ、湿潤状態のシリコーンフォームを得る工程である。
【００３２】
加熱温度は、通常５０～１００℃、好ましくは６０～８０℃である。加熱温度が該範囲内にあると、油層が硬化する前の水の揮発を抑制することができるため好ましい。加熱温度が、１００℃を越えると水が沸騰することにより、フォーム内に生成する気孔が粗大になるため好ましくない。加熱温度が、５０℃未満であると油層が硬化するのに長時間を要するため好ましくない。また、加熱時間は、通常０．５～１０時間、好ましくは０．５～３時間である。
【００３３】
第２工程を行うと、湿潤状態のシリコーンフォームが得られる。該湿潤状態のシリコーンフォームは、油中水滴型エマルション硬化原料の油層中のアルケニル基含有オルガノポリシロキサンとハイドロジェンオルガノポリシロキサンとがそのまま付加反応して硬化したものであるため、水層に由来する略均一な大きさの気孔を有するシリコーンフォームが得

られる。なお、シリコーンフォームは、上記のように界面活性剤として分子の両末端又は片末端のみが親水基で変性された親水性基変性オルガノポリシロキサンを用いるとシリコーンフォームの気孔構造が独立気孔構造になり易く、分子の側鎖が親水基で変性された親水性基変性オルガノポリシロキサンを用いるとシリコーンフォームの気孔構造が連続気孔構造になり易い。

【００３４】

第３工程は、湿潤状態のシリコーンフォーム中の水分を除去してシリコーンフォームを得る工程である。水分の除去には、通常用いられる乾燥機等が用いられる。硬化温度は、通常１００～１８０℃、好ましくは１２０℃～１６０℃である。

【００３５】

第３工程を行うと、シリコーンフォームが得られる。該シリコーンフォームは、気孔径が小さく且つ気孔径が略均一である。該シリコーンフォームの密度は、通常０．１０～０．８０ｇ／ｃｍ^2、好ましくは０．２０～０．４０ｇ／ｃｍ^{2}である。気孔の平均径は、通常５～１００μｍ、好ましくは１０～５０μｍである。また、該シリコーンフォームの空隙率は、通常１５～９０％、好ましくは２０～５０％である。ここで、空隙率とは、空隙の全体積を嵩体積で除した値をいう。

【００３６】

本発明で得られるシリコーンフォームは、例えば、緩衝材、断熱材等として使用することができる。

【００３７】

【実施例】

以下に実施例を示すが、本発明はこれらに限定されて解釈されるものではない。

【００３８】

実施例１

２５℃における粘度３５００ｃＳｔのアルケニル基含有オルガノポリシロキサン（信越化学工業株式会社製ＫＥ１０６）１００重量部、水３００重量部及び２５℃における粘度１３０ｃＳｔの片末端カルビノール変性シリコーンオイル（信越化学工業株式会社製Ｘ－２２－１７６ＤＸ）８０重量部をハイブリッドミキサ（キーエンス株式会社製）にて１５分間攪　した後、２５℃における粘度５００ｃＳｔのハイドロジェンオルガノポリシロキサン（信越化学工業株式会社製ＣＡＴ－ＲＧ）１０重量部を加え１分間攪　して、オルガノポリシロキサンが油層に含まれる液状の油中水滴型エマルション硬化原料を得た。なお、信越化学工業株式会社製ＫＥ１０６には、アルケニル基含有オルガノポリシロキサン以外に、アルケニル基含有オルガノポリシロキサンとハイドロジェンオルガノポリシロキサンとを付加反応させるに十分な量の白金族系触媒が含まれている。このエマルション硬化原料を鋳型に注入して７０℃で３時間加熱して付加反応させて硬化させた。この後、得られた湿潤状態のシリコーンフォームを、１５０℃の乾燥機中に２時間放置してシリコーンフォームを得た。該シリコーンフォームは独立気孔構造であり、密度が０．３９ｇ／ｃｍ^2、気孔の平均径が１５μｍであり、空隙率が６０％であり、硬化前後の体積変化率は－５％であり、硬化後に収縮した。ここで、体積変化率は、硬化後の体積から硬化前の体積を引いた値を硬化前の体積で除したものである。

【００３９】

実施例２

白金族系触媒の配合量を１重量部とし、水の配合量を３３０重量部とし、片末端カルビノール変性シリコーンオイル８０重量部に代えて２５℃における粘度１１０ｃＳｔの両末端カルビノール変性シリコーンオイル（信越化学工業株式会社製ＫＦ６００３）２５重量部及び２５℃における粘度１５０ｃＳｔの側鎖ポリエーテル変性シリコーンオイル（信越化学工業株式会社製ＫＦ６０１５、ＨＬＢ：４）２５重量部を用いた以外は実施例１と同様にして、クリーム状の油中水滴型エマルション硬化原料を得、実施例１と同様にしてシリコーンフォームを得た。該シリコーンフォームは連続気孔構造であり、密度が０．３５ｇ／ｃｍ^2、気孔の平均径が８０μｍであり、空隙率が６５％であり、硬化前後の体積変化

率は－３％であり、硬化後に収縮した。

【００４０】

比較例１

白金族系触媒の配合量を１重量部とし、水の配合量を３３０重量部とし、片末端カルビノール変性シリコーンオイル８０重量部に代えて２５℃における粘度１３０ｃＳｔの側鎖ポリエーテル変性シリコーンオイル（信越化学工業株式会社製ＫＦ６０１１、ＨＬＢ：１２）３０重量部を用いた以外は実施例１と同様にして、液状の水中油滴型エマルション硬化原料を得た。このエマルション硬化原料を実施例１と同様にし鋳型に注入して７０℃で３時間加熱して硬化させたところ、エマルション硬化原料中のオルガノポリシロキサンのみが塊状に硬化し、湿潤状態のシリコーンフォームは得られなかった。

【００４１】

【発明の効果】

本発明に係るシリコーンフォームの製造方法によれば、得られるシリコーンフォームは、気孔径が小さく且つ気孔径が略均一であり、剛性及び断熱性に優れる。また、該方法によれば、第２工程で油中水滴型エマルション硬化原料から湿潤状態のシリコーンフォームを形成する際の体積変化が小さい。このため、緩衝材や断熱材として好ましいシリコーンフォームを型による成形で容易に製造することができる。